Determination of Arsenic (III) and (V) Species in Some Environmental Samples by Atomic Absorption Spectrometry

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Abstract

A method for determination of arsenite As (III) and arsenate As (V) in some sediments and water samples was developed by using Hydride Generation-Atomic Absorption Spectrometry (HG-AAS). Optimization of the signal was carried out for a number of experimental parameters, including the carrier gas flow rate, sample volume, concentration of reducing agent; sodium borohydride (NaBH₄), and the concentration of hydrochloric acid (HCl). The precision for nine sample replicates was better than 3.1% for all arsenic species. The accuracy of the method was determined by analysis of a lake sediment reference material (IAEA-SL-1). This method can be applied for sediments and water samples.

Keywords

Arsenic Speciation; Hydride Generation Atomic Absorption Spectrometry (HGAAS); Water; and Sediments

Introduction

Arsenic is a natural contaminant in soil and water, and depending on its form it can be toxic at low levels. Arsenic is also present in the food chain, and it is widely known that fish contain various levels of both inorganic arsenic and organic arsenic species, such as axsenobetaine. Accordingly, determination of arsenic at low levels in water and sediments samples is very important. Arsenic is typically found in open ocean and coastal sea-water at concentration of 1-2 µg/L(Cullen et al., 1989). The level of arsenic in drinking water mostly does not exceed 5 µg/mL, while, arsenic occurs in normal soil at level from less than 1 µg/L to 40 µg/L. Arsenic is used in agriculture in pesticides and employed in different industrial processes such as production of semiconductors, glasses, pigments and textile printing (Baragagli et al.,

2002, Sloof et al., 1991, and Freitas et al., 1999b). Arsenic is found in inorganic forms: arsenite As(III), and arsenate As(V), and in organic forms such as monomethyl arsenic acid (MMA) and dimethylarsenic acid (DMA) (Fransconi et al., 1998). Inorganic arsenic compounds are highly toxic, while organic arsenic compounds are less toxic (Koch et al., 1999). Arsenic in environmental samples has been determined by Atomic absorption spectrometry (AAS) (Laborda et al., 1991, Chausseau et al., 2000, and Ebdon et al., 1998), Electrothermal Atomic Absorption (B'Hymer et al., 1998, Guerin et al., 1997, and Roig- Navarro et al., 2001), Hydride Generation-Atomic Absorption Spectrometry (HG-AAS) (Quijano et al., 1996, Magnuson et al., 1996, and Pantsar- Kallio et al., 1997), Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (Thomas et al., 1997, and Jackson et al., 1998), Ion Chromatograph (Guerin et al., 1997) and HG-ICP-MS. For analysis of arsenic by HG-AAS, the procedure involves the reaction of As(III) with the reducing agent NaBH₄ and HCl to produce volatile hydride arsine AsH_3 which is carried by argon gas flow to the optical cell where the arsine decomposes into As^0 atoms and finally is detected by photomultiplier tube detector (PMT). The main advantages of HG-AAS are the separation of the matrix, good reproducibility and increase in the detection limit of arsenic.

Methodology

Apparatus

Atomic Absorption Spectrometry-Vario 6, Analytical Jena GmbH, Germany, equipped with Hydride Generation and Hollow Cathode Lamp operated at 10mA was used for the determination of arsenic. A

spectral band width of 0.5 nm was selected to isolate the 193.7 nm As line. Table (1) shows the optimum experimental conditions for the determination of arsenic by HG-AAS.

TABLE 1 INSTRUMENTAL AND CHEMICAL CONDITIONS FOR THE DETERMINATION OF ARSENIC BY HG-AAS.

Wavelength	193.7 nm
Current	10 mA
Sample volume	5 ml
Delay time (sec.)	4 Sec.
Analysis time	20 Sec.
Measurement mode	Peak area
HCl concentration	3 %
NaBH4 concentration	1 %
Argon flow rate	200 ml/ min.

Reagents

All the used reagents were of analytical-reagent grade or higher purity and deionized water provided by a Milli-Q System was used. Reducing agents (aqueous solution of 0.3% sodium borohydride in 0.05% sodium hydroxide) were prepared freshly and filtered before use. Hydrochloric acid solution was prepared from 37% HCl (MERCK). Potassium iodide (KI) and ascorbic acid (MERCK). Stock standards solution (As) 1000 µg/mL was Merck reference solution. To avoid any contamination, all glass bottles were rinsed with concentrated nitric acid in a sub-boiling system followed by de-ionized water before use.

Sampling and Sample Preparation

Both four sediment and water samples were collected from different places in the area around the Egyptian Atomic Energy Authority (EAEA) as shown in Table (2).

In this work, two different methods were used for the soil samples digestion; the first by weighting 0.2 gm sample and adding 4 ml nitric acid 65% , 1ml Hydrogen peroxide 30 % and 3 ml of hydrofluoric acid 40 %; While the other by weighting 0.2 gm sample and adding 1 ml of Hydrofluoric 40% and 5 ml boric acid 5%. At the end of digestion process, the sample diluted with 18 mega ohm.cm de-ionized water. As(III) shows better sensitivity in the arsine generation process. It is preferred to reduce As(V) to As(III) with pre-reducing agent KI and Ascorbic acid. It has been found that the

digestion method using nitric acid and hydrogen peroxide produces nitrous oxides and the presence of oxidants affects the reduction of As(V) to As(III) and AsH_3 generation with $NaBH_4$ leading to smaller and lower signals. To avoid these effects, the digested samples were treated with ascorbic acid before treatment with KI and ascorbic. The use of the first method was recommended for the digestion of sediment sample. For generation and measurement of As, hydride operational parameters (concentration of $NaBH_4$, flow rate of $NaBH_4$, HCl concentration, sample volume, flow rate of argon as a carrier gas) were studied.

Results and Discussion

For optimization of the experimental parameters to achieve the best possible analytical performance, several experimental parameters were optimized, such as volume of sample injected, sodium borohydride and hydrochloric acid concentrations, and argon flow rate. These parameters were tested for both water and sediment samples.

The hydride technique involves the reaction of acidified aqueous samples with a reducing agent, such as $NaBH_4$. The $NaHB_4$/HCl reduction mixture generates hydrides as shown in the following reaction (Robbins et al., 1979).

$$NaBH_4 + 3H_2O + HCl \rightarrow H_3BO_3 + NaCl + 8H$$

$$E^{m+} + H \text{ (excess)} \rightarrow EH_n + H_2 \text{(excess)}$$
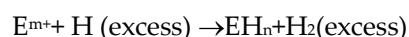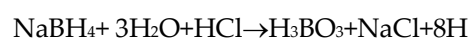
Where: E is the analyte of interest; m may or may not be equal to n

The produced hydrides are volatile transported to a quartz cell by means of an argon carrier gas, in which the hydrides are converted to gaseous metal atoms.

Accordingly, the argon carrier gas has a significant influence on sensitivity because, if the flow is too high, the atom or hydride cloud is dispersed too rapidly. If the flow is too low, the resulting signal and sensitivity are lower. Consequently, these parameters are effective for the efficiency improvement of the method so we must optimize our system for this parameter to have the optimum values of these parameters.

TABLE 2 SEDIMENTS AND WATER SAMPLES

Water Samples	Sediments Samples
In front of EAEA	From the deep of Ismailia Canal in front of EAEA
	From the side of Ismailia canal in front of EAEA
In front of Alum Factory	From the side of Ismailia Canal in front of Alum factory
In front of Fertilizer Factory	From the side of Ismailia Canal in front of Fertilizers factory
	From the deep of Ismailia Canal in front of Fertilizers factory
In front of Iron Factory	From the side of Ismailia Canal in front of Iron factory

TABLE 3 DETERMINATION OF TOTAL ARSENIC, As (III) AND As (V) IN (mg/kg) IN CERTIFIED REFERENCE MATERIAL BY HG-AAS

Sample	As(III)	As(V)= (Total As-As(III)	Total As Certified	Total As Measured
Lake Sediment IAEA-SL-1	22.12	7.33	24.7 – 30.5	29.45

Effect of Sample Volume

Different volumes from the samples in the range from 2 to 15 mL were used. Peak area was found to increase over the range from 2.5 to 10 mL for As, with a slight decrease in sensitivity at 15 mL, where it appears that the signal may reaching saturation. Although the current method using a 10 mL sample has sufficient sensitivity to be able to determine arsenic in unpolluted systems.

Effect of Concentration of NaBH₄

The effect of concentration of the reducing agent NaBH₄ in the range 1-5% was studied and the optimum concentration of NaBH₄ (1%) represented the best sensitivity of arsenic peak (Fig. 1). At 1% NaBH₄ concentration with different concentration of HCl (1–5%) gives high signal of As (III). Also at 1% NaBH₄ concentration with different concentration of HCl (1–5 %) gives not so high signal (5-10%) of As (V).
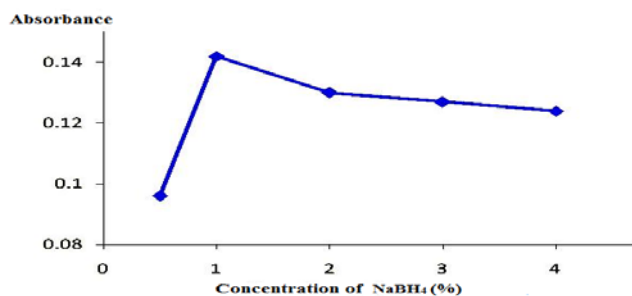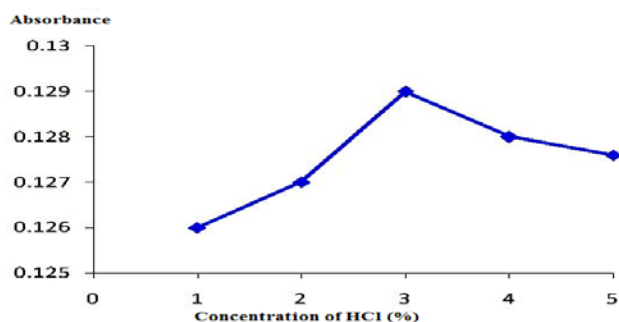

FIG. 1 VARIATION OF ABSORBANCE AT DIFFERENT CONCENTRATION OF NABH₄

FIG. 2 VARIATION OF ABSORBANCE AT DIFFERENT CONCENTRATION OF HCL

Effect of Concentration of HCl

HCl is acid medium in the generation of arsenic hydride. The effects of concentration of HCl and peak intensity of As were studied at range (1–5 %). The absorption signal of As (III) increases with increase HCl concentration in the range of 1–3% and then starts to decrease (Fig. 2). The best intensity of arsenic obtained shows that the optimum value of HCl concentration is (3%).

Effect of Argon Carrier Gas

Argon gas of high purity is used for carrying the arsine AsH₃ from the hydride generator to atomizer. The effect of argon carrier gas from the range (100 - 500ml/min.) was studied and the optimum value of argon flow rate is 200 ml/min, representing the best sensitivity of arsenic peak (Fig. 3).
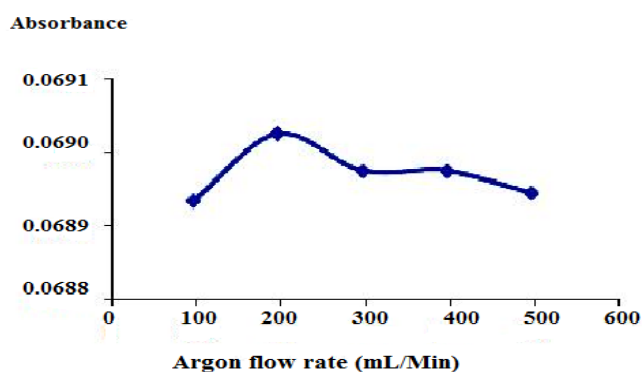

FIG. 3 VARIATION OF ABSORBANCE AT DIFFERENT FLOW RATE OF ARGON

Validity of Analytical Procedure

The calibration curve for As(III) solutions is linear from 0-5 mg/L as shown in Fig. 4. In order to investigate the possibility of measurement of As species in real samples, lake sediment, two certified reference materials were analyzed for As species using HG-AAS (Table 3).
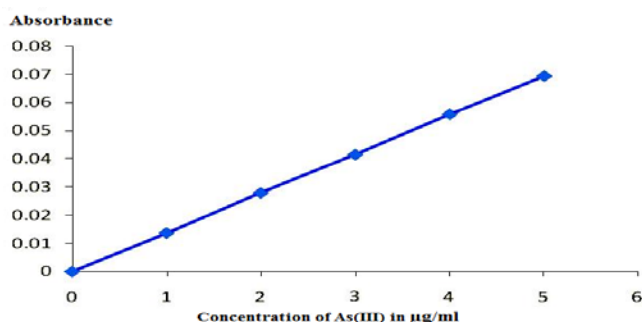

FIG. 4 CALIBRATION CURVE OF AS(III)

The sensitivity for As(V) to form hydride is very low (5-10%) so we cannot measure As(V) directly but its concentration is calculated as the difference between total arsenic and As(III), so we first measure the samples without and reduction with (KI and Ascorbic acid mixture), and it is As(III) concentration only, then

the sample is totally reduced to measure the total arsenic and the As(V) concentration can be calculated. Good agreement between the certified and measured values is reached for certified reference material indicating good accuracy of analysis. A series of water samples and soil samples collected from Ismaelia canal for analysis of As results was collected in Tables (4 and 5).

TABLE 4 DETERMINATION OF TOTAL ARSENIC, As (III) AND As (V) IN (μg/ L) IN WATER SAMPLES BY HG-AAS

Sample	As(III)	As(V)	Total As
1	3.72±0.25	2.12±0.14	5.84±0.20
2	4.12±0.41	1.58±0.09	5.70±0.25
3	8.24±0.21	3.05±0.18	11.29±0.20
4	14.43±0.28	3.37±0.21	17.80±0.25

TABLE 5 DETERMINATION OF TOTAL ARSENIC, As (III) AND As (V) in (mg/ kg) IN SOIL SAMPLES BY HG-AAS

Sample	As (III)	As (V)	Total As
1	26.55±1.22	6.15±1.11	32.70±2.17
2	39.30±2.27	11.75±1.24	51.05±2.25
3	44.70±2.21	12.10±1.28	56.80±2.26
4	51.10±3.24	5.90±0.29	57.00±2.17

Conclusions

- Sample digestion by microwave was fast, less contaminated and less chemicals consumptions.
- Atomic absorption spectrometry was a simple technique for determination of trace elements in water and sediments samples.
- Ion chromatograph was good technique for separation and determination of trace elements in short time with precise results.
- Hydride generation atomic absorption spectrometer was simple, fast and inexpensive technique for speciation of arsenic.
- Determination of concentrations of element species was more important than that of total element concentration.

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